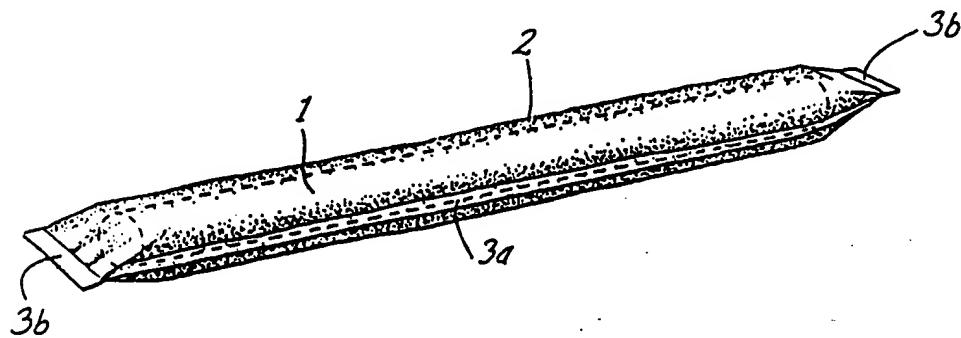




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54) Title: METHOD FOR THE PRODUCTION OF A CHEMICALLY BOUNDED CERAMIC PRODUCT AND A PRODUCT MANUFACTURED ACCORDING TO THE METHOD



## 57) Abstract

The present invention relates to a method for the production of a chemically bonded ceramic product by a reaction between one or several pulverulent binding agents as well as a liquid reacting with said binding agents. The ceramic product can also include one or several aggregate materials, which essentially do not participate in the chemical hardening reactions. According to the invention a powder body is compacted, which comprises said binding agent(s) and possibly aggregate materials without an addition of said liquid, by subjecting, before said raw compact is impregnated with said liquid, said powder body to such a high external pressure that a thoroughly integrated raw compact is obtained, in which the filling density has increased to at least 1.3 times the initial filling density, which is defined as that filling density, which is obtained by shaking, vibrating and/or carefully

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## METHOD FOR THE PRODUCTION OF A CHEMICALLY BONDED CERAMIC PRODUCT AND A PRODUCT MANUFACTURED ACCORDING TO THE METHOD

### TECHNICAL FIELD

The present invention relates to Chemically Bonded Ceramics (CBC), i.e. chemically bonded materials as compared to other advanced ceramics, which usually are made by a sintering process at elevated temperatures. More specifically, the invention relates to a method for the production of a chemically bonded ceramic product by a reaction between one or several pulverulent binding agents and a liquid which reacts with these binding agents. The ceramic product can also include one or several aggregates, which essentially do not react chemically with the other components. The invention also relates to the product manufactured according to the method.

### BACKGROUND ART

The CBC-materials are a very large and heterogenous group of materials, which include anything from concrete, based on a conventional Portland cement, to advanced ceramics in the dental field as well as in the orthopaedics, to name a few of the fields of application of the CBC-materials.

In the dental field mainly only materials, which cannot be called CBC-materials, have been used as permanent tooth fillings. Amalgams have been used primarily, which do not meet the high non-toxicity requirements for human use, which must be increasingly satisfied. Also, other materials for permanent tooth fillings, e.g. methyl methacrylate-based composites, which have a tendency to produce hypersensitivity reactions, are considered less suitable. Also, these plastic materials have substantial drawbacks due to the fact that they shrink after being applied and furthermore they display an unsatisfactory resistance to wear.

Hydraulic cements have also been used as dental filling materials. Thus, US-A-4 689 080 relates to the use of calcium aluminate as a binding agent for dental applications.

Another example of a material which can be called a CBC-material is the cement, which is used in the dental field and which is based primarily on zinc oxide and orthophosphoric acid. This cement has been used for temporary fillings, fastening of crowns etc., but its strength has so far been unsatisfactory and it can not be used as permanent fillings.

Another type of material used for dental applications are the so called glass polyalkenoate cements and similar materials. SE-B-381 808, EP-A-0024056 and EP-A-0115058 exemplify this type of material.

Generally, stiffening substances for dental or general orthopedic applications (implants) must meet several requirements in order to be rated as satisfactory and accepted substances, e.g. having hygienic and in the dental field also aesthetic properties. Also, these materials must not contain components, which are toxic or which in their environment can give rise to toxic substances. Furthermore, they must be functional, have mechanical properties designed for their field of use, be corrosion resistant, comfortable to use, be biological compatible, have an acceptable appearance as well as not be too expensive to use. An important property of a stiffening substance for dental applications on human beings is also that it stiffens slowly in order to make it possible to perform the desired application without great speed. On the other hand, such a stiffening material must comparatively quickly become sufficiently tough and sufficiently fastened in order to allow the treated person to eat a reasonably short time after the application. The above-mentioned hydration materials, zinc oxide-based materials, glasspolyalkeonate cement materials etc. satisfy these requirements for dental materials as regards i.a. hygienic

and aesthetic properties, toxicity etc. However, the strength of these materials is not considered sufficient in contrast to amalgams.

As is well known, the strength properties of the CBC-materials can be improved by various treatments of the components of the material or through additives of various types. Reinforcement of concrete by means of reinforcement bars is one example of this technique on a macroscale. Also, it is well known how to reinforce advanced CBC-materials by means of reinforcing fibers, which e.g. can be steel fibers, carbon fibers, glass fibers, organic fibers etc. However, feasible dimensions and treatment limitations constitute physical limits when choosing reinforcement materials and methods designed to be used in the dental care and surgery fields. Also, the requirements as to the surface smoothness of the stiffening material, its flow when prepared and applied and - when it is used as a cementum mass, i.e. as an adhesive - its joint thickness of less than 50  $\mu\text{m}$ , constitute an upper limit for the physical size of the reinforcing particles in connection with dental and surgical applications. Also, conventional reinforcing fibers might function, as to dental applications, as a footing for bacteria, provided they protrude from the surrounding matrix material and/or are not worn off concurrently with the matrix material.

It is known that the strength of at least some cement materials can be improved by compacting the paste of the pulvulent binding agent and the reacting liquid, which can be attained by means of a dispersant, more specifically a so called plasticizer (Science, Feb. 1987, pages 235-236 as well as US-4 363 667). When preparing the paste, which is done in connection with the application, the mass is homogenized and flaws are expelled through a repeated kneading. The method is statistical and isolated strength-impairing air pores may remain. Also, the homogenization in connection

Also, the degree of close packing and consequently the strength can be improved, provided the powder is composed of well-balanced grain-size fractions; US-4 353 746 and US-4 353 747. It is true that this technique per se can be a part of the technique according to the present invention, but it is not sufficient for obtaining the required results. Thus, merely inconsiderable strength improvements are obtained.

#### BRIEF DESCRIPTION OF THE INVENTION

The general object of the invention is to suggest a method for the improvement of the strength of chemically bonded ceramic products, so called CBC-products or CBC-materials.

A special object of the invention is to prepare the binding agent or binding agents as well as optional aggregates, of which the CBC-product will be composed, in such a way, that the user can have the use of a binding agent product, which is prepared to obtain the required strength and which the user finishes by impregnating the finished binding agent with the liquid either before the application or in situ.

According to one aspect of the invention one object is to suggest a material, which is suitable for dental applications, particularly for permanent fillings.

According to another aspect of the invention, one object is to suggest a material, which is suitable as a prosthesis material (implant) for general orthopedic applications.

According to another aspect of the invention one object is to facilitate an in situ addition of the hydration liquid (e.g. in the form of sea water) for underwater constructions.

These and additional objects can be attained by compacting a pulverulent body, composed of said binding agent(s) and optional aggregates, by exerting the pulverulent body to

such a high external pressure and at such a high temperature, that, without sintering reactions, during the compaction a well integrated raw compact is obtained, in which the filling density increases to at least 1.3 times the initial filling density, which is defined as that filling density, which is obtained by shaking, vibrating and/or carefully packing of the loose powder in a container, before the raw compact is impregnated with the liquid. The pulverulent body is preferably exerted to such a high pressure, that the filling density increases to at least 1.5 and suitably at least 1.7 times the initial filling density.

According to a first preferred embodiment of the invention said binding agent consists of one or several hydraulic binding agents, the hydration phases of which belong to the group of compounds, which consists of aluminates, silicates, phosphates and sulphates, the liquid being a hydration liquid, consisting of water and possibly substances dissolved in the water. The preferred aluminates is calcium aluminate, which can be present in various proportions between CaO and  $Al_2O_3$ . The preferred silicate is calcium silicate with varying proportions between CaO and  $SiO_2$ , which is the main component of Portland cement, which however contains also other components, e.g.  $Al_2O_3$ . Other phases are e.g.  $3 CaOx Al_2O_3$  and  $4 CaOxAl_2O_3$  and  $4 CaOxAl_2O_3xFe_2O_3$ . Combinations of silicates and aluminates having a higher portion of aluminate than in an ordinary Portland cement are also useful. Phosphates, which are useful as binding agents in this connection, are e.g. calcium phosphate and zinc phosphate and a useful sulphate is the essentially non-hydrated gypsum,  $CaSO_4 \cdot \frac{1}{2} H_2O$ .

The above-mentioned substances may exist as natural minerals or be produced synthetically. Irrespective of their origin they must be preliminarily treated according to conventional technique, which however does not constitute any part of the present invention. As a result of this

powder is obtained, in which the pulverulent grains have a size ranging from a submicron-size up to a maximum size of 100  $\mu\text{m}$  in the largest extension of the grains. An ordinary medium grain size can be as high as about 15  $\mu\text{m}$ , i.e. 50 percent by weight of the grains have a size larger than about 15  $\mu\text{m}$ . The shape is very irregular. Also, the pulverulent grains generally form large porous agglomerates. For these reasons and due to an electro-static interaction between the powder grains, a very low filling density in the loose powder is obtained with this type of powder. A normal so called TAP-density, also called Bulk-density or Loose-density for a calcium aluminate cement, e.g. of grade SECAR 71, is 32 %. This can be elevated to about 39 % by shaking the powder, vibrating it or exerting it to a careful packing in the container, used to store the powder. The filling density in the latter condition, i.e. subsequently to a vibration, a shaking or a careful compaction, which is seen as the initial filling density as regards the method according to the invention. However, the same can be additionally increased somewhat by impregnating the powder with a non-reacting liquid, which subsequently is removed previous to the very heavy compaction according to the invention.

It is true that the invention has been developed for hydration materials, e.g. aluminates, silicates, phosphates and sulphates, but the invention's principal features probably can be utilized also in other systems. In the dental field, and also in other fields, the invention can e.g. be utilized in case the binding agents mainly are one or several oxides, e.g. zinc oxide, while said liquid is one or several acids, e.g. a phosphorus-based acid, preferably and mainly orthophosphoric acid.

An additional feasible application field among several others is the production of a so called glass polyalkeonate cement, the binding agent possibly consisting of a mixture of a glass powder and a freeze-dehydrated acid according to

a technique known per se, while the liquid can be water.

Besides the binding agent and the liquid, which subsequent to the reaction with the binding agent forms a solid phase, it is possible, as is generally known, to add an aggregate material, i.e. a material which does not participate in the chemical reactions between the binding agent and the liquid but which is present as a solid phase in the finished, solid final product. For certain application fields such aggregate materials can be reinforcements of various types, e.g. fibers of metals, carbon, glass or organic materials etc. The reinforcement advantageously can be obtained by introducing long crystals, so called whiskers, e.g. of SiC,  $Si_3N_4$  and/or  $Al_2O_3$ .

Also, for dental applications or as a prosthesis material for general surgical applications the CBC-material according to the invention can include aggregate materials, provided they meet certain requirements. Thus, they must not be toxic, they must be biocompatible, must not cause irritations in the oral cavity in the case of dental applications, must not corrode etc. A small amount of boron nitride can e.g. be added to be used as a solid lubricant in connection with the compaction of the dry pulverulent material, preferably an amount of 5-15 percent by volume of the dry substance previous to the compaction and the impregnation with said liquid.

In case the binding agent is one or several hydration materials, the aggregate material can also be e.g. hydroxylapatite or solid solutions thereof and/or oxides of one or several of titanium, zirconium, zinc and aluminum and/or some prehydrated phase of the binding agent or binding agents. It is particularly advantageous to use as aggregates outwardly projecting, needle-shaped crystals, preferably of titanium dioxide, which are biocompatible and chemically inert in all the systems considered here.

such hydration liquids as phosphoric acid etc. Said titanium dioxide aggregate suitably comprises three-dimensionally oriented and star-shaped, needle-shaped crystals, the thickness of which can be a few tenths of a micrometer but the length of which normally is several times larger. These crystals are agglomerated to larger particles or agglomerates having a size of several micrometers. The reinforcement effect of the agglomerates in the hardened product is due to the nature of the agglomerates. Thus, the bond between the setting phase and the agglomerates of titanium dioxide crystals is improved and strengthened when the agglomerates are etched, e.g. in 0.5-10 M, particularly 1-3 M, sodium hydroxide or in another etch solution, e.g. a mineral acid such as phosphoric acid.

According to the invention a superplasticizer can also be admixed in a dry condition or by means of a water-free solution, subsequent to which the raw compact is produced. A suitable superplasticizer is e.g. 79 % hydrolysed polyvinyl acetate.

When the raw compact is impregnated with a liquid, it is important that not only a high but also a regular filling density has been obtained to avoid large pockets, which would be filled with the liquid, when the impregnation takes place. Thus, the mean value of the liquid content in the moistened raw compact has to be low, but also within every small sub-volume the liquid content has to be low. Nevertheless, the liquid content has to be sufficient in order to dissolve the binding agent to such a high degree, that it will not be present in large continuous bands throughout the finished CBC-material. In case the binding agent is an aluminate or another hydration material and in case the material is used as tooth fillings, then long continuous bands of non-reacted calcium aluminate would result in, when the filling gradually is worn off, a reaction between the aluminates and the water in the oral cavity in a not desirable way. However, the agg-

regates can be used as not only mainly reinforcement materials but also as agents conducive to an optimal distribution, a sufficient but not too high liquid content being available in every sub-volume for reaction with the binding agent, and consequently long continuous bands of non-reacted binding agent substance mainly being avoided. The aggregate particles or the agglomerates of aggregate particles preferably have a particle size of 0.5-10  $\mu\text{m}$ . It is particularly advantageous to let such particles have a mean particle size, which is considered smaller than the mean grain size of the binding agent, because then a somewhat higher initial filling density can be obtained. The amount of aggregate material is preferably 3-25 percent by weight of the finished CBC-material or 4-30 percent by volume of the mixture of the binding agent powder and the aggregate material in the raw compact.

In a special embodiment of the invention a fine-grained binding agent phase and a somewhat coarser aggregate material phase in the powder body are used instead. According to this embodiment the main portion of the powder grains in the binding agent phase can have grain sizes of 1-20  $\mu\text{m}$ , while the main portion of the grains of the aggregate material phase have a size distribution of 5-50  $\mu\text{m}$ . This choice of particle size distribution between the binding agent phase and the aggregate material phase will facilitate an almost total "consumption", i.e. a reaction between the binding agent phase and said liquid during the impregnation. Consequently, the final CBC-product will be composed of comparatively large aggregate material particles, surrounded by completely hydrated areas and areas reacted in a corresponding way respectively. Such a material can be particularly suitable for wear applications in wet and preferably in hydration-environments. In case non-hydrated areas are exposed to this wet, wearing environment, the wear may be accelerated due to the fact that a release from a non-hydrated phase is larger than for a thoroughly hydrated phase. A corresponding situation may exist when the binding agent is

non-hydration binding agent and the final product is designed for an environment, which contains a liquid of the same type as is used as a reaction-liquid for the hardening of the product.

The initial filling density, i.e. the filling density before the compaction according to the invention in a dry condition, is normally not higher than 40 %. By special treatment methods, e.g. through centrifugation in a chemically non-reacting liquid, the filling density can be increased to a maximum of 50-55 %.

According to a preferred embodiment of the invention the compaction according to the invention is carried out by a cold isostatic compaction. A cold isostatic compaction is an isostatic compaction carried out at such a low temperature, that no sintering reactions take place, normally at ambient temperatures. However, other types of mechanical pressing, e.g. cold-rolling or forging, preferably gradual forging, can also be used.

During the compaction the agglomerates of binding agent grains and possibly or preferably also the agglomerates of the used aggregate materials are disintegrated or crushed and the fragments are redistributed, the porosity decreasing and the material being homogenized. The process is facilitated, if the used powders are treated in a non-polar liquid, e.g. petroleum ether (light petrol), the binding force for the resulting agglomerates after the removal of the liquid being small, i.e. soft agglomerates being obtained.

When a cold isostatic compaction is used, the powder body is placed in an impermeable shell, suitably a plastic shell, subsequent to which the enclosed powder body is subjected to an external pressure in a liquid volume surrounding the shell, preferably a pressure higher than 200 MPa, preferably

not less than 250 MPa.

Another method of carrying out the cold compaction of the binding agent and the optional aggregates according to the invention is by means of injection molding or extrusion, the powder also containing a solid lubricant, i.e. a polymer in an amount, which roughly is equivalent to the pore volume of the raw compact. After the compaction the polymer lubricant is allowed to evaporate, suitably through evaporation by heating.

Irrespective of the type of compaction method used, the compaction is carried out in such a way that raw compacts are obtained having a geometrical shape adapted to the intended field of application. The raw compact can e.g., when it is designed for dental applications, be a thin string, possibly subdivided into easily separable sections, or small granules. In case the compaction is carried out as a cold isostatic compaction in a plastic shell, the raw compact suitably is kept encased in this shell up to the moment of application, particularly if the raw compact contains hydration-type binding agents, which compact otherwise would require a packing to prevent it from being unintentionally subjected to moisture during its transport and storage. A few suitable product embodiments are shown in the accompanying drawings, in which:

Fig. 1 shows a string of a raw compact in a plastic shell according to a first embodiment;

Fig. 2 shows a series of granule-shaped raw compacts in a long continuous plastic shell;

Fig. 3 shows a section III-III in Fig. 2; and

Fig. 4 shows a longitudinal section through a third possible embodiment of a raw compact in a impermeable plastic shell.

As regards the embodiment shown in Fig. 1, raw compact 1 simply comprises a straight even rod, which can have a circular or another cross-section and a thickness of ~ ~ ~

mm, if the material is designed for dental applications. The shell comprises a folded plastic film 2, which is longitudinally sealed along one of the sides of the shell, at 3a, and at its ends displays end seals 3b. The length of rod 1 can be e.g. 30-200 mm.

Granules 4 according to Fig. 2 and 3 have a more or less spherical shape and are placed in a plastic shell 5, which e.g. can be shrink-sealed around granules 4 before the cold isostatic compaction.

According to Fig. 4 raw compact 6 is instead designed as a rod, subdivided into sections 7 and weakenings 8 between the sections. An impermeable plastic shell 9 is used. Instead of shells 3a, 5 and 9 respectively made of a plastic material it is possible to use shells made of another polymer, e.g. rubber.

Subsequently to the compaction the intermediate product, obtained in this way, has developed a considerable bending strength and compression strength. Consequently, it is not easy to smash or break loose pieces of the raw compact. Thus, it is important that its size corresponds to the volume of the desired final product or that the individual raw compacts are sufficiently small or that the raw compact has been designed with indications of fracture, so that small pieces can be broken loose and so that the final product can be easily reconstructed from a plurality of small raw compacts subsequent to the admixture of said liquid. These possibilities are available by means of the shown embodiments, reference being made to Figs. 1-4.

The impregnation with said liquid, which will react with the binding agent, is done precisely when the CBC-product is to be used. The raw compact is then impregnated with the chosen liquid by moistening the raw compact with the liquid or by immersing the raw compact in the liquid. The

pores of the raw compact now will function as capillaries, which suck in a suitable amount of the liquid. Due to the partial disintegration of the binding agent the strength of the raw compact decreases drastically; from a compression strength of about 10 MPa to a compression strength of about 3 MPa. Consequently, the wet raw compact can now be broken and shaped into smaller pieces, if that is desirable. Consequently, due to its initial disintegration its workability will be acceptable and it can e.g. be used as a tooth filling material.

In case larger constructions are to be erected, a plurality of raw compacts can be impregnated and subsequent to the impregnation be joined together to large units. The invention particularly facilitates an in situ-adding of the liquid, particularly a hydration-liquid in case the binding agent is one or several hydration-binding agents. The liquid can in this case be e.g. sea water or water from lakes and streams for underwater constructions, the impregnation with water being carried out directly on the site of application.

In case the powder in the raw compact entirely comprises a binding agent, e.g. a cement material, then 30-60 % of the binding agent is dissolved by said liquid and is hardened by known reactions. The total dissolved amount depends on several factors, e.g. the size of the pulverulent grains, their shape and distribution, but also on the degree of compaction and the size of the raw compact are important in this respect, since the hydrates which are slowly formed will constitute diffusion barriers against additional water. The used aggregates can in this regard be utilized actively in order to maximize the hydration and the corresponding reaction respectively in case other binding agents than hydration-materials are used. If it is assumed that the filling density in the raw compact is e.g. 67 % or 2/3, 1/3 being pores, and assuming that 1/3 of the binding agent

is "consumed", i.e. is dissolved by the liquid during the impregnation, it would be theoretically feasible to obtain a complete hydration, provided half the binding agent was replaced with the same volume portion aggregate material.

In case the invention is to be used for the production of materials designed as permanent tooth fillings, the aggregate material preferably comprises needle-shaped titanium dioxide crystals, agglomerated to large particles having a size of 1-5  $\mu\text{m}$ , which has been described above. This aggregate material has a very high whiteness, opacity and albedo. Also, it is completely stable to light, chemically inert, biocompatible and does not cause irritations or other types of discomfort in the oral cavity as regards dental applications. This material comprises particles of pure titanium dioxide, comprising three-dimensional needle-shaped crystals having a star-shaped orientation. This material can be bought from e.g. TIL Central Laboratories, Stockton-on-Tees in Great Britain, under the trade name "Tilcom". The thickness of the crystals is a few hundredths of a nanometer, but their length is several times larger. They are agglomerated to particles having a grain size of 0.5-10  $\mu\text{m}$ .

Additional aspects of the invention are set forth in the following examples.

#### EXAMPLE 1

A calcium aluminate cement, grade Secar 71 (manufactured by Lafarge) was used as a binding agent phase. Secar 71 is a mixture of  $\text{CaOxAl}_2\text{O}_3$  and  $\text{CaOx2Al}_2\text{O}_3$ . The medium grain size was about 15  $\mu\text{m}$ . An amount of about 5  $\text{cm}^3$  of said binding agent powder was isostatically compacted in a cold condition at a pressure of 300 MPa in an impermeable plastic shell to obtain parallelepiped-shape. The filling density of the raw compact was measured to 67.5 % after the cold isostatic compaction. The plastic shell was removed and distilled water was added and the specimen was subsequently kept at 35°C

and a relative humidity (RH) of 100 % for 24 hours. The strength, determined in a three-point bending test, was measured to 70 MPa. The open porosity of the specimen measured according to an ASTM-method for porosity measurements was 1.7 %.

#### EXAMPLE 2

Secar 71 according to Example 1 was isostatically compacted in a cold condition as a block with the dimensions 4x4x8 cm<sup>3</sup> at 320 MPa, and a raw compact having a density of 2.10 g/cm<sup>3</sup> was obtained, which corresponds to a filling density of 70 %. The block compacted isostatically in a cold condition was cut up into a few test rods with the dimensions 40x3x3 mm. Distilled water was added, and substantially half of the specimens were kept in a moist environment (100% RH - relative humidity) and the rest in water at 37°C for varying periods of time. Results as to the obtained medium bending strength in MPa, the open porosity (OP) and shrinkage (K) are given in the following table.

TABLE 1

Specimen	1 day			7 days			120 days		
	MPa	OP %	K %	MPa	OP %	K %	MPa	OP %	K %
100 % RH	66	1.4	<0.1	58	1.4	<0.1	64	1.0	<0.1
water	65	1.9	<0.1	58	1.3	<0.1	65	1.0	<0.1

#### EXAMPLE 3

In this example a cement material called OPC was used (Ordinary Portland Cement). Consequently, the cement material mainly comprised calcium silicates, CaOxSiO<sub>2</sub> and a small portion aluminum oxide, iron oxide etc.

The cement powder had a medium grain size of about 10 µm. The powder was isostatically compacted in a cold condition at 300 MPa to a parallelepiped-shaped body having a volume of 30 cm<sup>3</sup>. The raw compact was impregnated with ordinary tap wa-

ter. The specimen was kept in water for 24 hours and subsequently the density and the bending strength were measured, with the following results:

TABLE 2

Specimen	Density g/cm <sup>3</sup>	OP %	Bending strength MPa
OPC	2.63	0.9	40 ± 4

## EXAMPLE 4

In this example a calcium aluminate of a type which is called Fondu (trade name) was used. The powder was isostatically compacted in a cold condition in the same way as in Example 3. However, the storage time in water was 7 days. In this case the raw compact was impregnated with tap water, and subsequently the specimen was treated in the same way as in Example 3, with the following results:

TABLE 3

Specimen	Density g/cm <sup>3</sup>	OP %	Bending strength MPa
Fondu	2.81	0.5	42 ± 2

## EXAMPLE 5

Cement powder of grade Secar 71, i.e. of the same type as in Example 1, was isostatically compacted in a cold condition at 300 MPa to a cube with the dimension 1 cm. Water was sucked into the specimen block, which subsequently could be disintegrated into granules with the dimension 1-2 mm. The granules were pounded before 2 minutes had elapsed at a pressure of 5 MPa to a new cube, which was hydrated for 24 hours at 35°C and 100 % RH, subsequent to which the compression strength was measured in a universal testing machine, type Instron. The compression strength was measured to 270 MPa.

## EXAMPLE 6

Synthetic calcium aluminate cement,  $\text{CaOxAl}_2\text{O}_3$ , was ground in petroleum ether and was screened through a sieve having a mesh size of 100  $\mu\text{m}$ . About 40 g of the powder were isostatically compacted in a cold condition at 300 MPa. To water and a superplasticizer (grade Gohsenol; 79 % hydrolysed polyvinyl acetate) dissolved in the water a portion of the specimen cube was added, while another portion of the specimen cube was centrifuged in the solution of water and superplasticizer at 6000 RPM. The specimen cube was not satisfactorily moistened without a centrifugation. The centrifuged specimen was crushed to small granules and was treated subsequently in the same way as in Example 5. The resulting compressing strength of the final specimen cube was measured to 230 MPa.

## EXAMPLE 7

A superplasticizer agent (grade Gohsenol) was added to an aluminate according to Example 6 and an admixture was carried out, partly in a dry condition and partly in a light petrol solution. Raw compacts were made of the powders by an isostatic compaction in a cold condition in a polymer tube. Water subsequently was forced through the tube. The tube was removed and the moistened mass was pounded to a parallelepiped with the dimensions 40x3x3 mm. The obtained bending strength in the hardened specimens was measured to  $49 \pm 7$  MPa in the two cases.

## EXAMPLE 8

To a cement raw material, grade Secar 71 (see Example 1), boron nitride (of a type which is sold under the name HC Starck), 5 percent by volume, was added. The boron nitride was a very fine powder, its grain fineness corresponding to a specific surface of  $3 \text{ m}^2/\text{g}$ . The mixture was isostatically compacted in a cold condition at 300 MPa. The obtained raw compact was impregnated with distilled water below  $30^\circ\text{C}$ . The moistened raw compact was subsequently crushed by subjecting it to a pressure of about 2 MPa. The granules ob-

tained in this way were pounded to a specimen block at a low pressure. This pressure was measured by a load sensor, connected to the pounder, which comprised a cylinder having a diameter of 2.5 mm. The workability, i.e. the required pressure to obtain an open porosity of not more than 2 % in a specimen, which has been hydrated for 24 hours at 35°C and 100 % RH, proved to be about 2 MPa lower than for the corresponding specimen without any admixture of boron nitride. This example shows that boron nitride functions as a lubricant when the moistened raw compact is shaped.

#### EXAMPLE 9

A cement raw material, grade Secar 71, according to Example 1, was mixed with 12 percent by volume fine-grained hydroxylapatite, which had a particle size less than 5  $\mu\text{m}$ , in a ball mill with petroleum ether and silicon nitride-cylpebs as a grinding agent (cylpebs = cylindrical pebbles; small cylindrical grinding pebbles). 8  $\text{cm}^3$  of the powder mixture was isostatically compacted in a cold condition at 300 MPa. The obtained raw compact was impregnated with a hydration liquid, comprising distilled water, tap water or water admixed with 0.5 % of soluble chloride salts. The hydration was allowed to continue for 24 hours at 35°C and 100 % RH, subsequent to which a bending strength testing was done according to Example 1. The mean strength of seven test rods was 61 MPa (the lowest value 42 MPa, the highest 93 MPa), which shows that a substantial amount of a fine-grained aggregate phase can be added without a substantial decrease in the bending strength (compare Example 1) and that the resulting strength mainly is not influenced by the degree of purity of the water, as far as this has been tested.

#### EXAMPLE 10

To a calcium aluminate cement of the same grade as in Example 1, Secar 71, was added 35 percent by volume of a polymer binding agent for injection molding, comprising a mixture of polyethylene and ethyl vinyl acetate. The mixture of

aluminate cement and polymer powder was homogenized in a mixer, type Brabender, and was injection molded at a pressure of 1200 bars to a parallelepiped. The polymer was subsequently vaporized by heating to 400°C. The filling density was then 65.5 %. The porous raw compact obtained in this way subsequently was impregnated with distilled water, admixed with 0.035 moles of a chloride salt and the moistened body was placed in water at ambient temperature. After a period of 24 hours its compression strength was 210 MPa. The rupture toughness of the material was measured by the impression method using a Vicker-diamond to 2.8 MPam<sup>2</sup>.

#### EXAMPLE 11

A calcium aluminate cement of the same grade as in Example 1, Secar 71, was ground for 48 hours and was sieved through a sieve having a mesh-size of 5 µm. A portion of the fine-sieved powder was hydrated in water for 24 hours and the powder was completely hydrated. The slurry was evaporated and a hydrated powder fraction was obtained. Similar amounts of the fine-sieved powder and the hydrated powder were subsequently admixed with the hydrated powder fraction. The mixture was isostatically compacted in a cold condition at 300 MPa. In the body obtained in this way the prehydrated phase is an aggregate material, because it can not react further with water. The raw compact obtained in this way can be impregnated with a hydration liquid in the way described in the examples above. The water which is sucked into the body essentially corresponds to the volume of the pore system and reacts with the non-hydrated calcium aluminate cement phase to the extent that after 24 hours essentially no non-reacted phase remains. In this way a volume increase due to a diffusion of additional water and consequently an additional hydration is prevented, which would mean a hydration above the available pore volume. By the process described in the example it is possible to obtain a final product having a bending strength of about 60 MPa.

## EXAMPLE 12

A gypsum powder -  $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$  - was compacted by an isostatic compaction in a cold condition at 300 MPa. The raw compact obtained a density corresponding to 66 % of the theoretical density. Water was subsequently added to it and it was hydrated for 24 hours. Ten specimen rods (35x3x3 mm) were cut. The strength was measured by the three-point bending test to 34 MPa (mean value; the lowest value 28 MPa and the highest 39 MPa). This strength exceeded the strength of ordinary gypsum more than five-fold. The density was 2.35 g/cm<sup>3</sup>, which is close to the theoretical maximum density, which is 2.32 - 2.37 g/cm<sup>3</sup>. This means that the porosity at least is less than 1 %.

The present invention can of course be varied within the scope of protection defined by the following patent claims and other substances than those described in the preceding description can of course be added. Thus, it is possible to add to the mixture of binding agents, a liquid and possibly aggregates also accelerators or retarders in order to speed up or suppress the hardening reaction.

## CLAIMS

1. Method for the production of a chemically bonded ceramic product by a reaction between one or several pulverulent binding agents as well as a liquid reacting with these binding agents, which ceramic product also can include one or several aggregate materials, which essentially do not participate in the chemical hardening reactions, characterized in that a powder body comprising said binding agent(s) and possibly aggregate materials without the addition of said liquid is compacted by subjecting, before impregnating said raw compact with said liquid, said powder body to such a high external pressure and at such a low temperature, that without sintering reactions when carrying out the compaction a thoroughly integrated raw compact is obtained, in which the filling density has increased to at least 1.3 times the initial filling density, which is defined as the filling density which is obtained by shaking, vibrating and/or carefully packing the loose powder in a container.
2. Method according to claim 1, characterized in that said powder body is compacted by mechanical pressing, preferably cold isostatic compaction.
3. Method according to claim 1, characterized in that said powder body also comprises an organic lubricant or binding agent, in that said powder body is shaped and compacted by injection molding or extrusion, in that said organic lubricant or binding agent is evaporated, a porous raw compact being obtained, and in that the raw compact obtained in this way is impregnated with said liquid.
4. Method according to any of claims 1-3, characterized in that said first binding agent is one or several hydraulic binding agents, the hydration phase belonging to that group of compounds, which comprises alumina

nates, silicates, phosphates and sulphates, and in that said liquid is a hydration liquid comprising water and substances dissolved in the water.

5. Method according to any of claims 1-3, characterized in that said first binding agent mainly is one or several oxides, preferably mainly zinc oxide, and in that said liquid is one or several acids, preferably mainly orthophosphoric acid.

6. Method according to claim 1, characterized in that said raw compact or a separate part of the same is impregnated with said liquid by allowing the liquid to be sucked into the body by capillary forces acting inside the body.

7. Method according to claim 1, characterized in that said raw compact or a part of the same is impregnated with said liquid partly by allowing the liquid to be sucked into the body by capillary forces acting inside the body and partly by centrifuging, shaking or vibrating said raw compact or said separate part or by subjecting said raw compact or said separate part to a similar treatment in the liquid.

8. Method according to claim 1, characterized in that when producing said raw compact the filling density is increased to at least 1.5 and preferably at least 1.8 times the initial filling density.

9. Method according to claim 1, characterized in that said compaction is carried out at a temperature less than 100°C, preferably at ambient temperature.

10. Method according to any of the preceding claims, characterized in that said raw compact is designed as a narrow string or a thin disc, possibly provided with fractal impressions.

11. Method according to claims 1-9, characterized in that said raw compact is shaped as granules.
12. Method according to any of claims 1-11, characterized in that said powder body is encased in a plastic shell and in that it is subjected to a cold isostatic compaction in a liquid in said plastic shell.
13. Method according to claim 1, characterized in that the optimal amount and content of said liquid depends on the degree of compaction and the corresponding amount of liquid, which by capillary forces is sucked into said raw compact.
14. Method according to claim 1, characterized in that a plurality of impregnated raw compacts are joined in order to build larger constructions.
15. Method according to claim 2, characterized in that said raw compact is hydrated in situ in a water environment, preferably for underwater constructions.
16. Method according to claim 1, characterized in that said powder body includes up to 50 percent by volume aggregates.
17. Method according to claim 16, characterized in that said powder body includes 5-25 percent by volume aggregates.
18. Method according to claim 1, characterized in that said powder body includes 25-50 percent by volume aggregates.
19. Method according to any of claims 1-18, characterized in that said binding agent is a hydration-binding agent and in that said aggregates completely or partly

ly are hydroxylapatite or solid solutions thereof and/or oxides of preferably titanium, zirconium, zinc and aluminum.

20. Method according to any of claims 1-19, characterized in that said powder body includes 5-15 percent by volume boron nitride.

21. Method according to any of claims 1-19, characterized in that said aggregates completely or partly are shaped as whiskers or fibers.

22. Method according to any of claims 1-19, characterized in that said powder body includes 5-20 percent by volume of a granulate, consisting of outwardly projecting, needle-shaped crystals of mainly titanium dioxide.

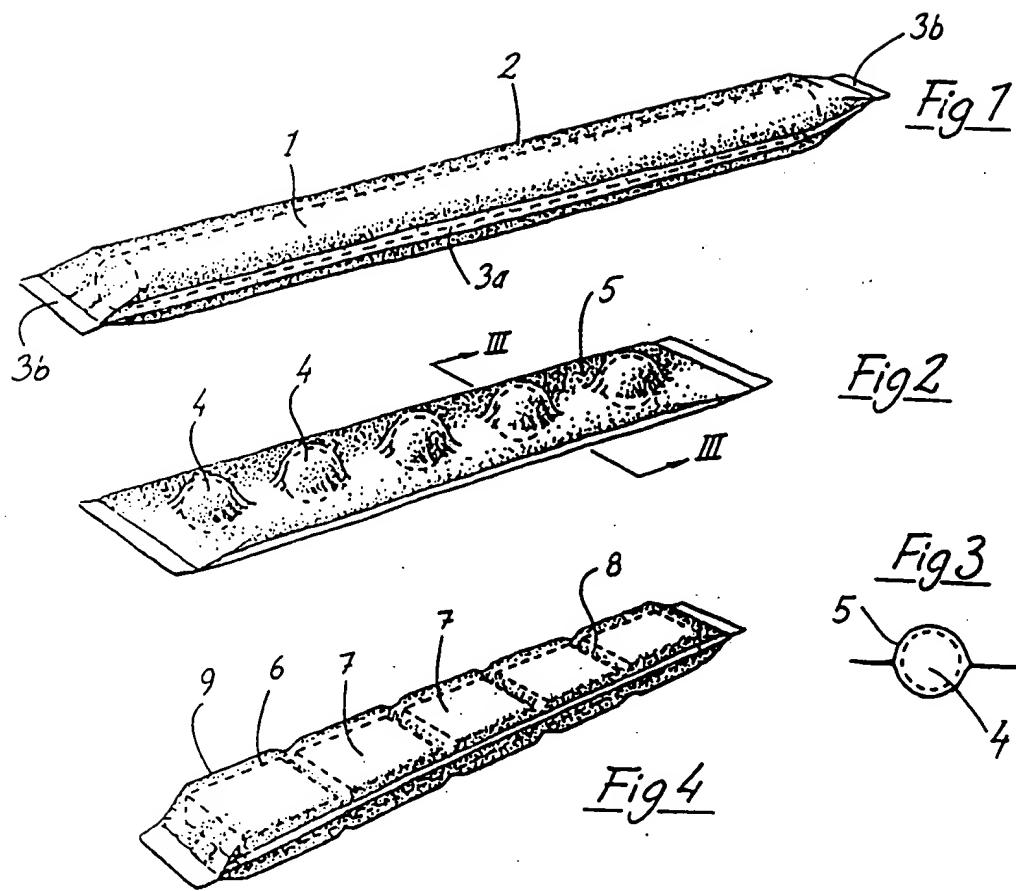
23. Method according to claim 22, characterized in that said titanium dioxide is etched.

24. Method according to claims 1-23, characterized in that said aggregate material comprises a material, which is more fine-grained than said binding agent phase and in that it preferably has a mean grain size of less than 10  $\mu\text{m}$ .

25. Method according to any of claims 1-23, characterized in that said aggregate material is coarser than said binding agent phase, more precisely in that said binding agent phase in said powder body mainly has a particle size of between 1 and 20  $\mu\text{m}$ , while said aggregate material comprises a powder having grain sizes mainly between 5 and 50  $\mu\text{m}$ .

26. Method according to any of the preceding claims, characterized in that a certain amount of a powder of the same type as said binding agent phase is hydrated

and subsequently is admixed with a non-hydrated pulverulent binding agent, and in that the powder mixture subsequently, possibly jointly with additional aggregate materials, is compacted, the prehydrated powder constituting an aggregate material in said raw compact.



# INTERNATIONAL SEARCH REPORT

International Application No. PCT/SE 90/00124

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC5: A 61 K 6/06		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC5	A 61 K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched <sup>8</sup>		
SE, DK, FI, NO classes as above		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	US, A, 4353746 (JAMES D. BIRCHALL ET AL.) 12 October 1982, see the whole document --	1-26
A	US, A, 4353747 (JAMES D. BIRCHALL ET AL.) 12 October 1982, see the whole document --	1-26
A	US, A, 4363667 (JAMES D. BIRCHALL ET AL.) 14 December 1982, see the whole document --	1-26
A	US, A, 4689080 (H. KAWAHARA ET AL.) 25 August 1987, see the whole document -----	1-26
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<p><sup>6</sup> Special categories of cited documents:           "A" document defining the general state of the art which is not considered to be of particular relevance          "E" earlier document but published on or after the international filing date          "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)          "O" document referring to an oral disclosure, use, exhibition or other means          "P" document published prior to the international filing date but later than the priority date claimed</p> <p><sup>7</sup> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention          "X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step          "Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art          "Z" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
7th June 1990	1990-06-13	
International Searching Authority SWEDISH PATENT OFFICE	Signature of Authorized Officer Jack Hedlund <i>Jack Hedlund</i>	

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.PCT/SE 90/00124

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the Swedish Patent Office EDP file on **90-05-07**  
The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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